

PACS numbers: 42.70.Ln, 68.35.bm, 72.40.+w, 73.50.Pz, 78.20.Nv, 82.35.Cd

Photoconductive Materials for Ordered Nanoobjects Based on Templates

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The purpose of this work is to study the properties of amorphous molecular semiconductors (AMSs), which are used as templates for the development of ordered nanoobjects. Photosensitive AMSs are carbazole-containing compounds for recording optical information in real time. They have high sensitivity and spatial resolution, and can work in automatic mode without an operator. It is important to improve the characteristics of AMSs and modes of their application. When optimizing the composition of AMSs, the most important problem is to find out the mechanisms of thermalization of carriers, the quantum yield in AMSs under photoexcitation, and the electrophysical phenomena. The technique of thermally stimulated depolarization is used for the analysis of these processes. This technique makes it possible to study the kinetics of the electric charge formed due to the orientation of permanent dipoles or the charge trapped by such deep traps as structural defects, impurity centres, charges accumulated at the interphase boundaries in the film. The spectral sensitivity is measured for the samples comprised of thin layers of carbazole-containing materials, which were produced by pouring toluene solutions. As found out, the quantum yield of photogeneration is decreased at higher wavelengths of light. A model based on the assumption of the Newtoni-

an nature of the dependence of the rate of energy loss for a non-equilibrium electron is proposed. Within the framework of this model, the dependences of the length and time of thermalization on the frequency of the exciting light, the temperature of the AMSs, and the parameter determining the rate of loss of excess energy by a non-equilibrium carrier of electric charge are determined. As a result, a phenomenological model of the electrophotographic process is proposed, and the composition of the AMSs is optimized. A template with an area of $\cong 4 \text{ cm}^2$ and a spatial period of $\cong 3\text{--}1 \text{ }\mu\text{m}$ is fabricated.

Метою даної роботи є дослідження властивостей аморфних молекулярних напівпровідників (АМН), яких використовують у якості темплатів для створення упорядкованих нанооб'єктів. Світлочутливі АМН є карбазолвмісними середовищами для реєстрації оптичної інформації у реальному часі. Вони мають високу чутливість, просторову роздільчу здатність, можуть працювати в автоматичному режимі без оператора. Актуальним є поліпшення характеристик АМН і режимів використання їх. Для оптимізації складу АМН найважливішим є з'ясування механізмів термалізації носіїв, квантового виходу під час фотозбудження АМН і перебігу електрофізичних явищ. Для аналізу цих процесів був використаний метод термостимульованої деполіризації. Він уможливорює вивчити кінетику електричного заряду, створеного під час орієнтації постійних диполів, або заряду, який захоплюється глибокими пастками у вигляді структурних дефектів, домішкових центрів, зарядів, накопичених на межі різних фаз плівки. В роботі проведено вимірювання спектральної чутливості зразків із тонких шарів карбазолвмісних матеріалів, одержаних за допомогою поливу толуольних розчинів. Встановлено, що зі збільшенням довжини світлової хвилі відбувається зменшення величини квантового виходу фотогенерації. Модель засновано на припущенні ньютонівського характеру залежності швидкості енергетичних втрат нерівноважним електроном. В рамках цього моделю одержано залежності довжини та часу термалізації від частоти збуджувального світла, температури АМН і параметра, що визначає швидкість втрати надлишкової енергії нерівноважним носієм електричного заряду. Отже, запропоновано феноменологічний модель електрофотографічного процесу й оптимізовано склад АМН, одержано темплат площею у $\cong 4 \text{ cm}^2$ з просторовим періодом у $\cong 3\text{--}1 \text{ }\mu\text{m}$.

Key words: amorphous molecular semiconductors, photosensitivity, electrophysical properties, electric charge.

Ключові слова: аморфні молекулярні напівпровідники, фоточутливість, електрофізичні властивості, електричний заряд.

(Received 25 January, 2023)

1. INTRODUCTION

Amorphous molecular semiconductors (AMSs) based on sensitized

photoconductive polymers have photoconductive properties in the visible and near-infrared wavelength ranges [1]. This is explained by the fact that the molecules of the sensitizer act not only as centres of light absorption, but also as centres (or their components) of photogeneration of charge carriers. These properties of AMSs make it possible to implement them in the development of microelectronic and information systems [1–4]. The AMSs based on poly(*N*-vinylcarbazole) (PVK), poly-*N*-epoxypropyl carbazole (PEPK), polyanthracene glycidyl ether (PAGE), poly(*N*-glycidyl carbazole) (PGK), carbazole-containing polyorganosiloxane (CCPO) are known and widely used. These AMSs are photosensitive due to the presence of carbazole cores, which have a large closed conjugated π -electron system, the regularity of their structure, and the close packing. As known [1, 2], the distance between the carbazole cores in various PVK (PEPK)–PGK–CPO structures gradually increases due to the increase in the number of atoms in the links of the main polymer chain, which connect neighbouring monomer links. The increase in the distance between the carbazole cores in the polymer chain leads to its higher flexibility and, at the same time, promotes the formation of charge transfer complexes (CTC). In the AMSs formed on the base of PGK and PAGE, the chain structure remains practically unchanged, and only the form of the donor dopant changes. The transition from carbazole donor cores to substituents with a longer bond system reduces the ionization energy of the donor and, therefore, leads to a wider spectral sensitivity of AMS.

The 2,4,7-trinitro (TNF) and 2,4,5,7-tetranitrofluorenone (TENF), 2,4,7-trinitro-9-dicyanomethylenefluorene-4-carboxylic acids, tetracyanoquinodimethane (TCNQ), 2, 7-dinitroundecylic acid ether, and the C₆₀ and C₇₀ fullerenes are used as sensitizers. The use of these AMSs allows synthesizing photosensitive materials that have spectral sensitivity in almost the entire range of visible light.

As known [1, 2], the photogeneration process in this type of AMSs includes several stages, and two main stages can be distinguished. The first one lasts approximation 10^{-11} – 10^{-12} s. At this stage, a neutral exciton-like state forms after absorption of a quantum of light, which transforms due to autoionization into an ion, *i.e.*, into a ‘hot’ pair of charge carriers. This ‘hot’ pair loses its excess energy due to inelastic interaction with neighbouring atoms, and is separated by the thermalization length r_τ during the thermalization time t_τ .

The thermalization process can be considered complete, when the excess energy of an unbalanced pair of charge carriers decreases to a value ΔW , at which the interaction with the environment becomes elastic [3]. The thermalization leads to the transition of a mobile charge carrier from the photogenerating centre to the carbazole

molecule of AMSs, which results in the formation of the electron-hole pair, that is, in thermal equilibrium with the environment.

Then the second stage starts. During this stage, the dissociation of the electron-hole pair occurs in the process of diffusion drift of charge carriers. This stage can be adequately described by the Onsager model [1, 2, 4], which takes into account the possibility of tunnelling. However, the Onsager model is not applicable to describing the first stage of the charge generation process in the AMSs, since it cannot be applied to describe thermodynamically non-equilibrium systems. The experimental studies of such a multistage process of photogeneration of electric charge carriers in the AMSs is rather difficult, as it is possible to measure only the consequence of all stages (for example, the quantum yield of photogeneration or luminescence). Theoretical research allows analysing each stage separately.

The aim of this work is to study the dependence of the thermalization length in carbazole-containing AMSs on the wavelength of the excitation light, and to develop and improve an adequate model of the process of thermalization of charge carriers during formation of ordered nanoobjects using templates.

2. EXPERIMENTAL TECHNIQUES

Free carriers of electric charge in AMSs form after a chain of separate elementary processes each of which affects the photogeneration. The results of all these separate elementary processes are experimentally recorded; each of these processes is determined by its own parameters (which are determined by the characteristics of the AMSs), and therefore they depend on the experimental conditions in different ways.

When studying the process of photogeneration of electric charge carriers in AMSs, the dependence of the quantum yield of photogeneration on the wavelength of the excitation light is of particular interest. This is explained by the fact that this dependence is mainly determined by thermalization, not by all processes that determine the photogeneration process.

The dependence of the quantum yield of photogeneration η in anthracene and pentacene, as well as in carbazole-containing compounds, was studied in [1, 2, 4–6]. It was shown there that the quantum yield of photogeneration of charge carriers increased at higher frequencies of absorbed light. According to the obtained experimental data on the photoprocesses in pentacene and the Onsager model describing the mechanism of electron-hole pair dissociation, it was concluded that the thermalization length of charge carriers increases with an increase in the frequency of the excitation light.

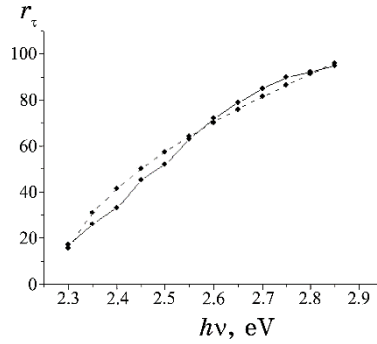


Fig. 1. Experimental [1] (solid) and theoretical (dashed) curves for the dependence of thermalization length in pentacene on the energy of excitation quantum.

This conclusion is illustrated in Fig. 1, which shows the experimental curve plotted according to the data of [1, 5].

It was shown in [1] that the spectral dependence of the quantum yield of photogeneration of charge carriers in polymer semiconductors near their light absorption edge could be described by the approximate relation:

$$\eta(\hbar\omega) \approx C(\hbar\omega - E_G^{ad})^n, \quad n \approx \frac{2}{5}, \quad (1)$$

where C is a function of temperature and electric field, and E_G^{ad} is the width of adiabatic energy gap.

It should be noted that there is no acceptable model that would substantiate Eq. (1).

Additional investigations into the dependence of the quantum yield of photogeneration of carriers, $\eta(\lambda)$, for a wider range of AMSs have been carried out. In these studies, samples with a thickness of 1.4–1.5 μm were used; the film was deposited on a glass substrate with electrically conductive SnO_2 sublayer by means of pouring toluene solution by standard method [7].

The surface of the sample was charged with positive ions in a corona discharge using the method of thermally stimulated depolarization of AMSs [8, 9] (Fig. 2). The surface potential was measured by the dynamic probe method. The spectral sensitivity S_λ was determined by the 20% drop in the potential of the AMSs free surface under 0.1 mW/cm^2 radiation. Prior to the measurements, the AMSs free surface had been charged to a potential of 190 V. The scheme of the experimental study of the kinetics of thermally stimulated relaxation of the surface potential of the template based on amorphous molecular semiconductors (AMSs) is shown in Fig. 2, *a, b*.

Figure 3 shows the experimental results on the thermal relaxation of the potential on the AMSs surface, which was charged in darkness by a positive corona discharge (anode under a high poten-

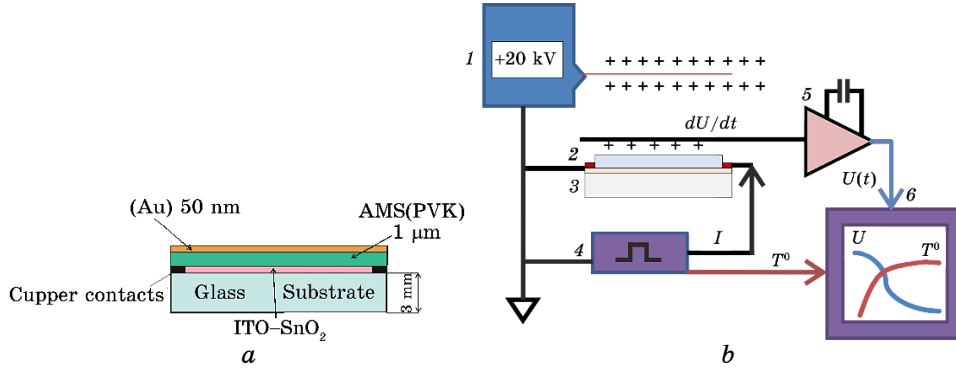


Fig. 2. Template structure and device for forming charge in AMSs bulk by thermally-stimulated depolarization: *a*—template structure; *b*—1 is the activator, $U_k = 20$ kV, charging time $t_{ch} = 3$ s, $d_{electrode} = 30$ μ m, 2 is the probe for measuring the potential of AMSs free surface; 3 is the template structure (from bottom to top: glass substrate, conductive layer (ITO, $R = 10$ Ohm/square) with copper electrical contacts, AMSs layer), 4 is the unit for temperature measuring and AMSs heating with pulse current and $t_{pulse} \leq 100$ ms, where the resistance of ITO layer is used as the sensor of AMSs temperature, 5 is the integrator on the operational amplifier with integration constant $t = 10$ s, and 6 is a personal computer with analog-digital signal input-output devices.

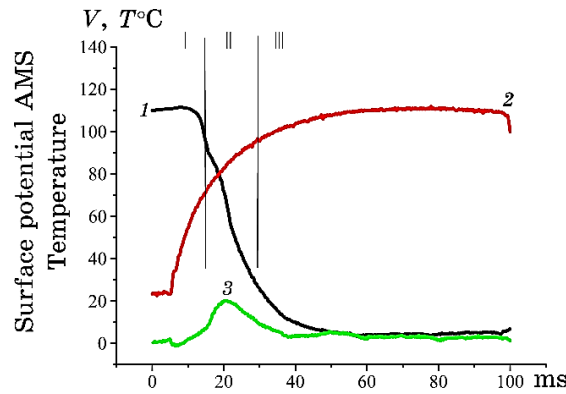


Fig. 3. Kinetics of relaxation of AMSs surface potential after charging the AMSs layer in corona discharge *1* (Fig. 2, activator): *1*—thermal relaxation of AMSs surface potential; *2*—temperature kinetics of AMSs layer; *3*—thermal relaxation of surface potential of polarized AMSs layer.

tial, $\varnothing = 30 \mu\text{m}$). The corona discharge was accompanied by a purple glow (corona). In such a corona, primary electrons are released at the outer boundary of the ionizing zone because of the gas photoionization by photons generated inside the corona.

These electrons are accelerated in the anode field, collide with gas atoms and ions and excite them, generating electron avalanches by shock ionization. In the outer zone of the discharge, the current is carried by positive ions. The positive space charge formed by them moves towards the AMSs and settles on its surface. The surface charge field reached $120 \text{ V}/\mu\text{m}$.

At the initial stage of AMSs heating (up to $T = 65^\circ\text{C}$), some increase in the surface potential is observed. There is a sharp drop in the surface potential of AMSs at 65°C (T_{cr1}), which ends at $T \cong 92^\circ\text{C}$ (T_{cr2}). The AMSs layer absorbs light in the visible range of the spectrum. Therefore, the thermal relaxation of the surface potential of a pre-polarized AMSs film was investigated. The electric charge was applied on the AMSs film surface in a corona discharge in darkness at 20°C , and the AMSs was heated up to 65°C for 20 ms (curve 2 in Fig. 3); then, the AMSs film was cooled down to 20°C and irradiated with $5 \text{ W}/\text{cm}^2$ light with a wavelength of 470 nm for 20 s. The relaxation of additional charge in the irradiated AMSs occurred. Then, the AMSs film was heated up to $T = 109^\circ\text{C}$ for 100 ms (curve 3 in Fig. 3).

The increase in the AMSs surface potential upon heating (curve 3 in Fig. 3) indicates the relaxation of the negative charge that has been formed in the AMSs bulk due to the dipole polarization of the AMSs during the primary heating. The relaxation peak of the potential of negative charge in the AMSs bulk is at 82°C . An approximate estimate of the activation energy of the volume charge capture centres using formula $W = Ak_B T$ gives $W \cong 0.03 \text{ eV}$ ($A = 1$).

Thus, the thermal relaxation of the electric potential on the surface of carboxyl-containing polymers based on a AMSs film shows that the film structure changes within $\cong 15 \text{ ms}$ in the temperature range of 65°C , and a negative charge forms on the traps in the AMSs bulk in the range of 65°C (T_{cr1}) $< T < 92^\circ\text{C}$ (T_{cr2}) during $\cong 10 \text{ ms}$.

The peak of the relaxation of negative charge potential in the AMS volume is observed at 82°C . The produced template can be used repeatedly below 65°C without aromatic solvents for several years, provided it is stored in an airtight container.

A localized charge was formed in the nanocomposite film by the electrophotographic method [8, 9], when the sample was exposed to a hologram using the three-beam scheme. The registration of holograms on the nanocomposite film consisted of three main stages. The sample with the nanocomposite film was placed near the anode

of the corona device in an air atmosphere. Due to the deposition of ions on the film surface in darkness, a uniformly distributed positive surface charge was formed. The potential of the film surface was 120 V.

The intensity distribution in the exposing light field forms the topology of the template. The simplest light field in the form of a two-dimensional lattice is implemented by means of two interfering laser beams. The angle between the beams determines the phase shift and, therefore, the spatial frequency of the grating. It is possible to form a light field of a certain class of symmetry with a predetermined intensity distribution by changing the number of laser beams, their relative directions in space, and additional modulations of amplitude or phase transparencies. In our experiments, three laser beams directed on the substrate along the lateral surface of a 25° regular cone were used for the template exposure.

When a nanocomposite film is exposed to light in the electric field of a flat capacitor formed by an electrically conductive substrate and surface charge, the photogeneration of current carriers occurs and photoconductivity appears [8, 9]. The current density of photoconductivity is determined by the modulated intensity of the light field that exposes the film surface. Because of the flow of photocurrents, the potential of the film surface decreases accordingly. A non-uniform distribution of the surface charge is formed on the surface after the exposure is completed. The surface charge density is modulated by the exposing light field. The field of surface charges modulated in space can deform the surface of the film during its softening.

The time of the surface relief formation was < 0.1 s. The reproducibility of the characteristics was ensured by the automation of the hologram registration process using the control module [8, 9]. When photocurrents flow through the film, charge carriers can also be trapped by deep traps that leads to the formation of localized volume charge modulated by the exposing light field. The probability of carrier trapping is determined by the density and energy characteristics of deep traps, which, in our experiments, were formed, apparently, during the deposition of the nanocomposite by co-condensation in a vacuum. Therefore, it is possible to form not only a relief (relief template), but also trapped charge (electret template) in those locations where the film is irradiated. The density of the localized electric charge is modulated proportionally to the intensity of the light field in the exposing hologram and, therefore, has the same topology.

The absorption spectra of the samples were recorded using a C-26 spectrophotometer. The experimental results are illustrated by the data given in Table. It contains the results of the study of the spec-

TABLE. Spectral sensitivity, absorption coefficient, and quantum yield of photogeneration of electric charge carriers in AMSs at two radiation wavelengths. The I_d is the AMSs ionization potential, and E_a is the electron affinity energy of sensitizer [1].

PP	Sensitizer	Sensitizer content		$Sdv/v = 0.2 \text{ m}^2/\text{J}$		$k(\lambda), \%$		Change in η when λ decreasing from 700 to 550 nm	E_a
		wt. %	$\lambda = 700 \text{ nm}$	$\lambda = 550 \text{ nm}$	$\lambda = 700 \text{ nm}$	$\lambda = 550 \text{ nm}$	$\frac{S_{550}}{S_{700}} : \frac{\kappa(550)}{\kappa(700)}$		
$I_d = 7.6 \text{ eV}$	TNF	3.0	0.16	3.0	20	60	6	2.05	
	TENF	5.0	1.2	8.0	40	75	3.4	2.35	
	TNFDC	3.0	3.0	6.0	60	85	1.5	2.60	
$I_d = 7.6 \text{ eV}$	TNF	3.0	0.15	5.0	10	70	5.2	2.05	
	TENF	5.0	1.3	7.0	46	78	3.4	2.35	
	Ud-DDPA	4.0	3.0	8.0	55	70	2.1	2.45	
	TENFDCM	3.0	3.5	7.0	60	80	1.6	2.6	
	TCHDN	1.0	1.0	1.2	65	85	1	2.7	
$I_d = 7.4 \text{ eV}$	TNF	4.3	0.4	5.0	10	75	2	2.05	
	TENF	4	1.0	5.2	60	80	4	2.35	
	TENFDCM	3.6	2.0	2.0	70	75	1	2.60	
	TCHDN	1.0	0.8	0.8	50	70	0.9	2.70	
$I_d = 7.1 \text{ eV}$	TNF	4.0	1.1	2.3	27	31	2	2.05	

tral dependences of S_λ on the potential decay rate 0.2 ($Sdv/v = 0.2$), the absorption coefficient of the sample $k(\lambda)$, the quantum yield of photogeneration of carriers $\eta(\lambda)$, and the electron affinity energy.

According to the data in Table, the dependence of the quantum yield of photogeneration on λ (or the energy of a quantum of light W_{ph}) increases at lower electron affinity energy of the sensitizer. This nature of the $\eta(\lambda)$ dependence can be qualitatively understood, taking into account that the initial energy of a hot electron W_e (neglecting the contribution of polarization effects) can be estimated as $W_{ph} - I_d + E_a + U$ (where U is the potential energy of the hot electron). In this case, the relative change in $\Delta W_e/W_e$ with a change in W_{ph} is determined by the ratio $\Delta W_{ph}/(W_{ph} - I_d + E_a + U)$, and this ra-

tio increases at lower E_a . It is worthwhile to note that, if this simplified analysis is correct, then, we should obtain for the C_{60} fullerene as acceptor (which has the characteristic value $E_a = 2.65$ eV) a composite, in which the quantum yield of photogeneration of charge carriers is almost independent on the light wavelength in the absorption range.

3. PHENOMENOLOGICAL MODEL OF THE THERMALIZATION PROCESS OF HOT CHARGE CARRIERS

The long-term studies of the processes of thermalization of photoexcited carriers of electric charges in AMSs [1, 2, 5, 6, 10, 11] (determination of the magnitude orders for time and length of thermalization, the ratios between the general properties of phonon spectra and t_τ and r_τ , the relationship between t_τ and the diffusion coefficient of charge carriers, *etc.*) have yield significant results. Nevertheless, the regularities of the thermalization process have not been clarified. This situation is mainly explained by the fact that this is a non-equilibrium process. This leads, for example, to the fact that a charge carrier during the thermalization cannot be characterized by such equilibrium parameters as diffusion coefficient or mobility. When developing thermalization models using quantum mechanical characteristics, one is faced with the difficulties of studying the relevant Hamiltonians and incomplete information about the values of the interaction cross sections.

We proposed a phenomenological model of the thermalization of hot charge carriers, which allows describing the dependence of the characteristics of this process on the wavelength of the exciting light and the environment temperature. The model is based on the assumption that the excess energy of a hot non-equilibrium charge carrier reduces due to its transition to neighbouring molecules with a rate that depends on the temperature difference between the hot electrons and the environment. It is assumed [1] that the thermalization process stops, when the energy of hot charge carriers decreases to the values, when the processes of inelastic interaction with the environment become impossible. This becomes possible when the temperature of the hot carriers exceeds the ambient temperature T_0 by a small amount of ΔT . It is also assumed that the potential energy of the interaction of a hot particle with the environment does not change during the thermalization process, and external fields are either absent or low, and therefore, do not affect the thermalization.

In this approach, the excess energy of a non-equilibrium charge carrier is determined by its kinetic energy or temperature. This allows determining the speed of movement of a non-equilibrium elec-

tron $v(t)$:

$$v(t) = \sqrt{\frac{3k_B T(t)}{m}}, \quad (2)$$

where k_B is the Boltzmann constant, and m is the mass of the non-equilibrium charge carrier.

According to the assumption that the charge carrier motion is rectilinear during thermalization, the thermalization length can be determined, using the following relation:

$$r_\tau = \int_0^{\tau} v(t) dt = \sqrt{\frac{3k_B}{m}} \int_0^{\tau} \sqrt{T(t)} dt. \quad (3)$$

The process of loss of excess energy by a non-equilibrium electron is determined by its interaction with phonons. The phonon spectrum is determined by the AMSs structure and has not been sufficiently studied. In such cases, it may be helpful to use the phenomenological models [7, 10], which allow explaining the dependences observed in the experiment and to obtain information about the microprocesses occurring in the AMSs.

Let us assume that the thermal transition process is Newtonian, that is, the thermal transition coefficient is proportional to the temperature difference $T(\tilde{t}) - T_0$. Then, the temperature kinetics of a non-equilibrium charge carrier is described by the following equation:

$$\frac{dT(t)}{dt} = -\frac{2\chi}{3k_B} (T(t) - T_0), \quad (4)$$

where χ is a parameter that determines the rate of excess energy loss by a non-equilibrium hot electron. The value of χ should usually depend on both the shape of the phonon spectrum and the characteristics of the interaction of the non-equilibrium electron with the sample molecules. However, it should be considered as a constant in further analysis.

As an initial condition, it is assumed that $T(0)$ is determined by the energy $\hbar\omega$ of the absorbed light quantum and the work A , which is necessary to create an excited state. The parameter A should depend on the values of I_a , E_a , and the energies of polarization transformations:

$$T(0) = \frac{2}{3k_B} (\hbar\omega - A). \quad (5)$$

Note that the relation (4) is a partial case of a more general ex-

pression

$$\frac{dT(t)}{dt} = -\alpha(T(t) - T(0))^n, \quad (5a)$$

where the parameter n is determined by the phonon spectrum, and the dimensional coefficient α determines the intensity of heat flow.

The solution of Eq. (4) under condition (5) has the following form:

$$T(t) = T_0 \left(1 - \exp\left(-\frac{2\chi}{3k_B} t\right) \right) + \frac{2}{3k_B} (\hbar\omega - A) \exp\left(-\frac{2\chi}{3k_B} t\right). \quad (6)$$

Using equation (6) and the following condition,

$$T(t_\tau) = T_0 + \Delta T, \quad (7)$$

we get an expression for the thermalization time t_τ :

$$t_\tau = \frac{3k_B}{2\chi} \ln \left[\frac{1}{\Delta T} \left(\frac{2(\hbar\omega - A)}{3k_B} - T_0 \right) \right]. \quad (8)$$

According (3) and (8), the radius of thermalization is

$$r_\tau = \sqrt{\frac{2}{m} (\hbar\omega - A)} \frac{3k_B}{\chi} \left[1 - \sqrt{\frac{\Delta T}{\frac{2}{3k_B} (\hbar\omega - A) - T_0}} \right]. \quad (9)$$

Expressions (8) and (9) allow finding the relationship between t_τ and r_τ regardless of the unknown parameter χ :

$$r_\tau = \frac{2\sqrt{\frac{2}{m} (\hbar\omega - A)}}{\ln \left(\frac{1}{\Delta T} \left(\frac{2(\hbar\omega - A)}{3k_B} - T_0 \right) \right)} \left[1 - \sqrt{\frac{\Delta T}{\frac{2}{3k_B} (\hbar\omega - A) - T_0}} \right] t_\tau. \quad (10)$$

4. DISCUSSION

When analysing the obtained results (formulas (8), (9), and (10)), it is necessary to take into account that the length of thermalization is not directly measured in the experiment. The r_τ -value can be determined using the information about the quantum yield of photo-generation η using the model describing the process of hole-

electron pair dissociation. Thus, when applying the traditional Onsager model, the information about r_τ can be obtained from the data [5, 8, 12], using the following relation:

$$\begin{aligned} \eta(h\omega) &= \\ &= \frac{\Phi_0}{2\gamma\langle r_\tau \rangle} \exp\left(-\frac{r_c}{\langle r_\tau \rangle}\right) \sum_{m=0}^{\infty} \frac{(r_c/\langle r_\tau \rangle)^m}{m!} \sum_{n=0}^{\infty} \left[1 - \exp(-2\gamma\langle r_\tau \rangle) \sum_{k=0}^{m+n} \frac{(2\gamma\langle r_\tau \rangle)^k}{k!}\right], \end{aligned} \quad (11)$$

where Φ_0 is the quantum yield of the primary autoionization process, and r_c and γ are

$$r_c = \frac{e^2}{4\pi\epsilon\epsilon_0 k_B T}, \quad \gamma = \frac{eE}{2k_B T}, \quad (12)$$

where ϵ is the dielectric constant of the medium, ϵ_0 is the vacuum permittivity, and E is the external electric field.

Analytical analysis of the dependence of r_τ as a function of $\eta(h\omega)$ resulting from relation (11) is complicated [5]. Numerical analysis shows that, all other conditions being equal (temperature, electric field), a higher value of the quantum yield is provided by a larger initial distance between the pair charges. This means that the experimental increase in the photogeneration quantum yield at higher frequencies of the absorbed light indicates an increase in the thermalization length of the electric charge carriers.

According to formula (9), r_τ increases at higher $h\omega$ (or lower λ); this is in good agreement with the obtained data summarized in Table 1 and the results of [1, 6]. A comparison of expression (9) with experimental data obtained for pentacene in [1] is shown in Fig. 1. The good correlation between the theoretical and experimental curves confirms the adequacy of the proposed model for the thermalization process. Note that the dependence $r_\tau(\lambda)$ also agrees with the results of the model, which assumes the loss of excess energy of the non-equilibrium charge carriers due to the collisions with surrounding molecules [3, 13]. It also follows from expression (9) that the length of thermalization increases with a decrease in the ambient temperature, which has been observed experimentally [2, 5].

Thus, the proposed model of the thermalization of charge carriers qualitatively explains the spectral and temperature dependences of the thermalization length and the quantum yield of photogeneration of electric charge carriers, and determines the ratio between r_τ and t_τ , which is in accordance with experimental results.

5. CONCLUSIONS

The experimental studies of quantum yield of photogeneration of

electric charge carriers in PVK, PEPK, PAGE, PGK sensitized with electron acceptors (TNF, TENF, Ud-DDPA, TENFDCM, and TCHDN) indicate a significant dependence of the quantum yield of photogeneration on the wavelength of the excitation light.

A phenomenological model of the process of thermalization of charge carriers in organic molecular semiconductors is proposed. The model has an exponential parameter, which specifies the dependence of the rate of 'heat flow of a hot charge carrier' on the temperature difference between the hot charge carrier and the environment, as well as the proportionality coefficient, which determines the heat flow by the temperature difference. The main suggestions of the model are the assumptions that the thermalization process is complete, when the excess energy of an unbalanced pair of charge carriers decreases to such a value that their interaction with the environment becomes elastic, and the rate of excess energy loss by hot charge carriers is proportional to the temperature difference between non-equilibrium charge carriers and the environment.

When using the Onsager model (or its modifications), the given model of thermalization makes it possible to qualitatively explain the spectral and temperature dependences of the quantum yield of charge carrier photogeneration.

A light-controlled template is developed, which consists of a transparent substrate ($d = 3$ mm, 40×40 mm), an amorphous molecular semiconductor (AMS, $d = 1$ μm), and a gold metal film ($d < 100$ nm). The mechanisms of its formation by means of electrophotographic process are determined. It is shown that the light field and electric charge that is formed in the AMSs bulk determine the relief and field topologies of the template. The maximum spatial capacity of the template is determined by the volume charge in the AMSs and is approximately 30 nm.

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